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ANORTHITE CLAY FORMULATION AS CATALYST FOR BIO-DIESEL PRODUCTION

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Abstract

Non-edible crude Karanj (Pongamia pinnata) oil (CKO) with high free fatty acid (FFA) content was used as effective renewable feedstock for fatty acid methyl ester (FAME) production. Calcium feldspar clay, a rare compositional variety of plagioclase clay, a low cost, abundant Earth resource, containing over 90 % CaO and belonging to the class of anorthite clay was used as heterogeneous catalyst in direct conversion of high FFA crude karanj oil to fatty acid methyl esters. The efficiency of the catalyst was made possible by the structural rearrangement of the mixed metal oxides' content of the catalyst at prolonged high temperatures. This behaviour is characteristic of glass transitions and properties of amorphous phases of plagioclase feldspar clay. This way, they were transformed into solid acid particles such as acidic mesoporous aluminum silicate mixed oxides. Optimum FAME yield of 98.97 % was obtained at 4 h reaction time, 6 wt% catalyst loading, 9:1 methanol to CKO molar ratio and at methanol reflux temperature. More than 90 % catalyst was recovered after four runs which still exhibited strong activity after further calcination at 500 °C for 1 h after each run. From the result of transesterification, non-edible, high FFA crude CKO is a potential renewable feedstock for the production of FAME using thermally treated, low cost, anorthite clay-derived catalyst.

Keywords: Anorthite clay; Fatty acid methyl ester; Crude karanj oil; Transesterification.

Introduction

Heterogeneous acid catalysts such as zirconium oxide (ZrO_2), zinc oxide (KF/ZnO) [1, 2], titanium oxide (TiO_2), tin oxide (SnO_2), zeolite oxides [2], sulfonic ion-exchange resin, sulfonic modified mesostructure silica, sulfonated carbon-based catalyst and heteropolyacids (HPAs) have been found effective in bio-diesel production. Also, the following heterogeneous alkaline catalysts such as calcium oxide (CaO), potassium phosphate oxide (K_3PO_4) and mixed oxides ($Ky(MgCa)_{2x}O_3$ [3], have been found invaluable in biodiesel production as a result of many challenges presented by homogeneous acid and base catalysts. For instance, heterogeneous catalysts are non-corrosive and environmentally benign [5], presenting fewer disposal problems, with easier separation and recovery of products, catalysts and the co-product [6]. Thus, solid base catalysis are economically and ecologically important fields in catalysis and the replacement of liquid bases with heterogeneous catalysts is becoming more and more important in the chemical industry [7].

The need for biodiesel production at competitive pump price with petro-diesel has prompted the recent search for biodiesel production from cheap or low cost resources for both feedstock and catalyst materials. Clay constitutes about 60 % of the Earth's crust and therefore a very abundant natural resource. Varieties of clay minerals abound with varying chemical compositions and have been applied as catalysts for esterification and transesterification [8]. Few attempts in the application of clay-based catalysts for biodiesel production were made by Manut Jaimasith and Satit Phiyanalimat who impregnated Suratthanee black clay (SB) and Ranong kaolin (RK) with CaO and concluded that at short reaction time [9], calcium oxide impregnated on Renong kaolin had better catalysis performance in the transesterification of palm oil over that of Suratthanee black clay [9]. Also, Olutoye and Hameed (2013), obtained 96 % FAME yield from waste cooking oil using iron-rich local clay catalyst characteristic of montmorillonite [10.11]. There is no record so far, however, of the application of clay-based catalyst for direct conversion of high FFA crude karanj oil to fatty acid methyl ester. This is the reason why we have selected the Ca-rich natural clay-based catalyst, calcium feldspar clay, for direct conversion of high FFA to produce FAME.

Moreover, since it is estimated that 70- 85 % of the cost of bio-diesel is determined by the cost of feedstock mainly from alone; and from edible oils such as soybean oil [12] , rapeseed oil [13], sunflower oil, safflower oil [14], jatropha oil [14], canola oil, palm oil , kernel oil

[15], beef tallow and fish oil, the competition for edible oils for food and for biodiesel production has made oil prices incredibly high. The result is the high cost of both food and biodiesel. Hence, current research is focusing mainly on low cost heterogeneous catalyst formulation and non-edible sources of feedstock such as used cooking oils, yellow greases, brown greases and fats, Oils and grease (FOG) recovered from sewer pipes and waste water treatment pipes [16].

It is therefore reported in this contribution, the use of non-edible, high free fatty acid crude karanj (Pongamia pinnata) oil (CKO) as an effective renewable feedstock in direct conversion to fatty acid methyl ester (FAME), using a novel, low cost, naturally abundant, Ca-rich clay-based heterogeneous catalyst (anorthite clay mineral).

Materials and methods

Materials

Calcium-rich clay (Calcium Feldspar clay) was obtained from Xuzhou Sushang Chemical Technology in Shanghai, China. The clay was in powdered form and was used as supplied without further modifications. CKO was sourced from Telaga Madu Resources Sdn. Bhd., Malaysia. Methanol (99.9%) and GC grade n-hexane of A.R. grade were purchased from Merck, Germany. Methyl heptadecanoate used for GC internal standard, 99.5% came from Sigma-Aldrich, Malaysia. The CKO was merely filtered to separate suspended matter while the rest of the chemicals were used without further treatment.

Catalyst preparation and characterization

10g of clay were charged into ceramic crucibles and placed into a muffler furnace for calcination at temperatures ranging from 500- 900 ^{o}C for 4 h at 4 ^{o}C/min ramping temperature. Calcined catalysts were stored in sample bottles, labeled according to their calcination temperatures such as CaF-600, CaF-700, etc, for calcium feldspar clay calcined at 600 ^{o}C, 700 ^{o}C, etc while CaF-Raw stands for the raw catalyst and all were placed in a desiccator.

Preliminary runs of transesterification reactions showed the catalyst calcined at 800 ^{o}C as having the best activity, all characterizations were based on this catalyst to save cost. The first step was to determine the strength of acid and basic sites of CaF-800 after calcination using temperature programmed desorption (TPD) technique in a Micromeritics AutoChem 2920 II equipment. A quatz reactor was loaded with 50 mg of catalyst and dried over He gas flowing at 400 ^{o}C for 1 h which was followed by a dry He sweep for 1 h. On cooling to 100 ^{o}C, the sample was exposed to NH_3/He gas mixture (90 vol. % He) for 1 h to make room for NH_3 to be adsorbed by sample. The sample was degassed of NH_3 by flushing with pure He to allow for accurate detection of desorbed NH_3. The measurement of NH_3 in sample was done by simply heating the sample to 850 ^{o}C at a heating rate of 10 ^{o}C/min over He gas while the desorbed NH_3 molecules were detected accordingly. The same process was repeated using CO_2 gas to determine the Basic strength. In comparison, surface acidity and basicity tests were carried out for CaF-800 using acid base titration technique with NaOH and HCl in accordance with procedures recorded in literature, and results obtained were correlated with results from temperature programmed desorption technique.

The developed catalyst (CaF-800) and the raw clay catalyst (CaF-Raw) were subjected to textural characteristics to determine the surface area and pore volume using Brunnauer Emmett Teller (BET) method over Micromeritics ASAP 2020 surface area and porosity analyzer (Micromeritics Instruments Corporation, USA) at 77 K using liquid nitrogen. The sample was thoroughly degassed at 200 ^{o}C before measurement began.

Powder X-ray diffraction (XRD) patterns were acquired on Philips PW 1710 X-ray powder diffractometer over $10^{o} \leq 2\theta \leq 90^{o}$ using Cu Kα radiation (λ=1.5406^{o}) at 40 kV and 40 mA at a scan rate of 0.02 ^{o}/min.

Scanning electron microscopy (SEM) was performed on the catalysts to determine the morphology and to analyze the porous structure of catalysts using a Zeiss Supra TM 35 VP scanning electron microscopy (Zeiss, Jena, Germany) coupled with FEI as a source of electrons accelerated at 300 kV. Energy-dispersive X-ray (EDX) spectroscopy was performed simultaneously with SEM to determine the catalyst surface composition.

Catalytic reaction

The catalytic activities of catalysts were tested by their application in the conversion of high free fatty acid (FFA) crude karanj oil (CKO) with methanol to fatty acid methyl ester (FAME). A set of four glass reactors, comprising 250 ml round-bottomed flasks equipped with spiral glass condensers placed on heating mantles with magnetic stirrers and thermostats were used for the transesterification reaction. In each run using crude karanj oil (CKO), 36.81 g of methanol and 3.4 g of calcined catalyst (CaF-800) were firstly mixed to homogeneity and refluxed at 65 ^{o}C for 0.5 h as the catalyst activation step. Then, 113.19 g of crude karanj oil was added to transesterify between 1-7 h reaction time. The weight ratio among methanol: catalyst: CKO was 11:1:33. At the end of reaction time, the reaction was allowed to cool to room temperature to allow for complete separation of glycerol and ester layers. The product was decanted to obtain the FAME layer, centrifuged at 3000 rpm for 10 mins and sent for Gas Chromatographic (GC) analysis. Over 90 % of the clay catalyst material could be recovered after each run, as some of it dissolved in the reaction process with methanol. The dissolved catalyst was recovered from product by centrifugation followed by filtration before GC analysis of product. Meanwhile, the recovered catalyst was washed severally with warm water, dried at 80 °C for 6 h and re-calcined at 500 °C for 1 h at 4 °C/min ramping temperature in a muffle furnace. The calcined catalyst was re-used 4 reaction cycles with a minimum yield of 88.67 %.

Results and Discussion

Catalyst characterization

Fig. 1 shows the scanning electron micrographs of both raw (CaF-Raw) and calcined (CaF-800) calcium feldspar catalysts, at 3.00 k x magnifications (bars at lower left equal to 2µm). Amorphous, prismatic, massively disordered, wood-like structure was observed for raw calcium feldspar (CaF-Raw), while more spherical morphologies with fine particles showing visible pore openings are demonstrated for the catalyst calcined at 800 °C (CaF-800).

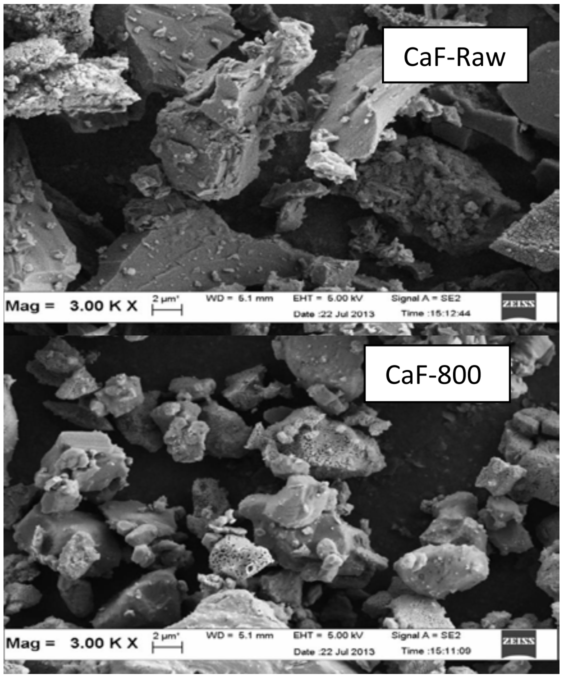

Fig. 1: SEM images of (a) CaF-Raw and (b) CaF-800 at 3.00 k x magnification.

From elemental compositions (Table 1), verified by using energy dispersive X-ray (EDX) detector, calcined calcium feldspar catalyst (CaF-800) was observed to contain over 80-90% by mass of calcium atoms with over 90 % of the calcium in the form of calcium oxide.

Table 1: EDX result of calcined catalyst, CaF-800.

Element	Wt%	At%
Oxygen	11.60	24.74
Calcium	88.40	75.26

Further investigation by chemical composition analysis revealed the presence of other metal oxides Table 2. Such metal oxides include Al_2O_3 (1.1070 wt %), MgO (2.3025 wt%) and SiO_2 (3.5204 wt%), among others. The presence of the metal oxides in calcined catalyst is attributed to increased active sites, which were never present in raw catalyst, for catalyst activity. The metal oxides [18], under prolonged calcination temperature, transformed into mixed metal oxides similar to mesoporous aluminum silicate mixed oxides, expected to produce the overall acidic character needed for direct conversion of high free fatty acid- crude karanj oil to produce fatty acid methyl ester [19].

Table 2: Results of SFP (BULK) Semi-quantitative Analysis of CaF-800.

Compd	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	Cr_2O_3	MnO
%by wt	2.30	1.11	3.52	0.008	0.028	0.011	0.35	91.911	0.035	0.029	0.015

The above attribute was corroborated by the work of Lin and co-workers [17]. which opined that, whereas many currently known base catalysts were destroyed by the presence of high free fatty acids, the kiln dust catalyst system could conveniently convert, even animal fats and various restaurant oils directly to biodiesel. This they said, could take place in the presence of an alcohol simply by adding an acid such as an acidic mesoporous aluminum silicate mixed oxide [18]. Acidic mesoporous aluminum mixed oxides can be used as a solid acid to sequester alkaline materials in a reaction mixture. Clay catalysts could also act as molecular sieve used as drying agents to help facilitate the esterification or transesterification reactions, in addition to helping to preserve the recyclability of the catalysts [18].

Table 3: BET results of CaF-Raw and CaF- 800

	CaF-Raw	CaF-800
BETsurface area, m^2/g	1.162	9.386
Pore volume, cm^3/g	0.0023	0.0445
Average pore size, Å	78.00	189.66

BET results of raw (CaF-Raw) and calcined (CaF-800) catalysts are presented in Table 2. A primary requirement of an ideal solid catalyst for biodiesel synthesis is large interconnected pores that would minimize diffusion limitations of molecules with long alkyl chains. A typical triglyceride molecule has a diameter of approximately 58 Å. It follows that the poor catalyst performance of CaF-Raw could be attributed to its low textural characteristics with surface area of 1.1624 m^2/g and pore volume of 0.0023 cm^3/g as against the improved textural characteristics observed in calcined clay catalyst (CaF-800) with surface area increasing by over 13% on thermal treatment and the pore size increasing by over 42% thereby justifying improved catalyst performance of CaF-800 over CaF-Raw.

Fig. 2 is the powder X-ray diffraction plots of CaF-800 and CaF-Raw catalysts showing the major phase compositions. The major crystalline phases in the catalysts include Calcium oxide (CaO), calcite ($CaCO_3$), Hatrurite (Ca_3SiO_5), aragonite ($CaCO_3$), Calcium Aluminium oxide ($CaAl_2O_4$) and Calcite Magnesium ($Mg_{0.03}Ca_{0.94}$)(CO_3), etc. Though clay is a complex material and the main peaks of XRD patterns are usually overlaid to one another, CaF-800 and CaF-Raw existed as hexagonal crystals $CaCO_3$ located around the region $2\theta = 29^{o}$- 48.5^{o}. However, a change in crystal phase was observed at elevated pretreatment temperatures as catalyst was transformed to more active calcite, syn. $CaCO_3$. The intense peak observed at $2\theta = 29.5^{o}$ was attributed to $CaCO_3$ present in both CaF-Raw and CaF-800. The presence of the $CaCO_3$ peak in the catalyst after calcination, though with a major drop in intensity, is attributed to incomplete evolving of molecules of CO_2 and organic matter by thermal treatment after initial calcination at 800 °C. This was in good agreement with the DTA findings by Sharma and co-workers on the weight loss observed in eggshell re-calcined at 700 °C, which was attributed to remaining $CaCO_3$ decomposition and loss of organic impurities after initial calcination at 900 °C. While adsorbed CO_2 and water molecules were evolved at about 250 °C to 650 °C, further treatment at higher temperature served to transform oxygen anions and metal cations into more active centers.

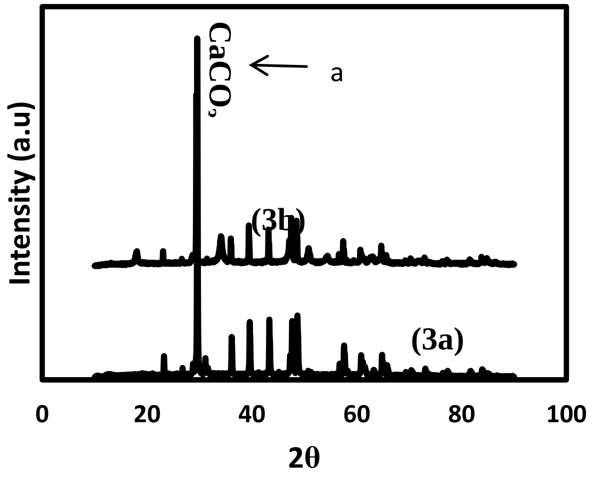

Fig. 2: XRD patterns of CaF-Raw (3a) and CaF-800 (3b).

Fourier transform-infra-red (FT-IR) spectroscopy, as an effective tool for a semi-quantitative estimation of structural information in complex solids is used to investigate the functional groups in the catalysts. The result of FTIR of CaF-Raw and CaF-800 was captured in the spectra (Figure not shown). The distinctive broad band at 3444.87 cm^{-1} observed in both CaF-Raw and CaF-800 were attributed to the O-H stretching, indicative of the high amounts of water adsorbed on the catalyst surface. While that of CaF-Raw appeared at 34.45 %T, the peak in CaF-800 appeared at 17.74 %T suggesting that much of the physisorbed water molecules were evolved by calcination and the O-H stretching in the calcined material may be attributed to chemisorbed water molecules. The bands at 1415 cm^{-1} and 1608 cm^{-1} were attributed to carbonate species while the bands at 1114 cm^{-1}, 1053 cm^{-1} and 883 cm^{-1} are characteristic of TO_4 tetrahedral groups (T= Ca, Al, Si) and are similar to 875 cm^{-1}, 806 cm^{-1} and 702 cm^{-1} in the raw catalyst. Also the band at 1114 cm^{-1} is associated with T-O bond asymmetric stretching vibrations (this bond provides information on the degree of crystalinity of sample, while the one centered at 883 cm^{-1} was associated with T-O bond internal deformation vibration.

The FTIR result was in good agreement with XRD patterns presenting with crystal monoclinic Hatrurite (Ca_3SiO_5), triclinic calcium silicate (Ca_3SiO_5) and monoclinic calcium aluminum oxide ($CaAl_2O_4$) containing the elements, Ca, Al, Si and O characteristic of anorthite clay with molecular formula $CaAl_2Si_2O_8$. The bands of T-O bond at 702 cm^{-1}, 808 cm^{-1} and 875 cm^{-1} present in the raw catalyst were weaker bonds and shifted to 883 cm^{-1}, 943 cm^{-1} and 1067 cm^{-1} in the calcined catalyst respectively and are attributed to the bending vibration modes indicating that new bonds were indeed formed by the catalyst pretreatment at higher temperature resulting in structural rearrangements to give more active species. The stretching vibrations due to –OH groups of water molecules adsorbed on the catalyst surface could be partly responsible for the bands at 1608 cm^{-1}, 3444 cm^{-1} and 3633 cm^{-1}. Nevertheless, the band at 3633 cm^{-1} could be partly attributed to the out - of - plane stretching vibrations and phase symmetric stretching of T-O-T which were considered to be the active sites of the basic species.

Effect of calcination temperature

From the results of transesterification of CKO using calcium feldspar catalysts calcined at various temperatures (Fig.3), it was observed that raw clay catalyst (CaF-Raw) gave very low conversion of triglycerides to FAME while thermally treated clay catalysts showed improved performance with increase in calcination temperature with optimum FAME yield of 98.97% recorded at 800 °C. The low catalyst activity observed for the catalysts treated at temperatures below 800 ^{o}C were due to the saturation of the catalyst pores with CO$_2$, water and other volatile matters which occupied available active sites meant to be centers of reaction and only partially removed at lower calcination temperatures.

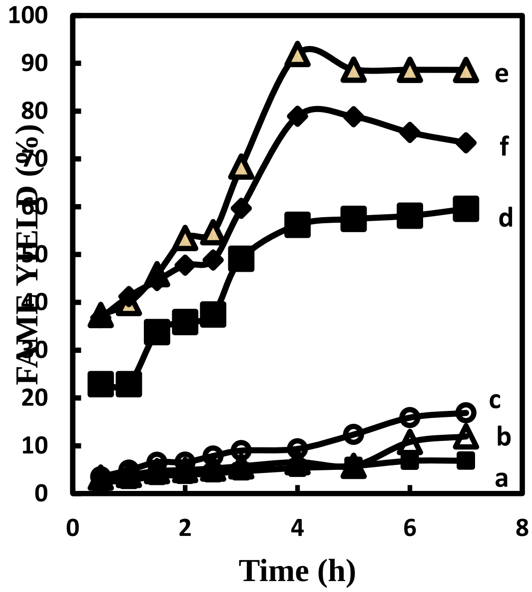

Fig. 3: Effect of calcination temperature on catalyst activity (methanol/oil mole ratio 9:1; catalyst loading/oil weight ratio 6 wt%; reaction time 4 h; reaction temperature 65 ^{o}C and stirring speed 700 rpm). Catalytic activities at various temperatures of calcination are represented by the graphs above as follows: a = raw sample, b = calcination at 500 ^{o}C, c = 600 ^{o}C, d = 700 ^{o}C, e = 800 ^{o}C and f = 900 ^{o}C.

To obtain high activity of alkaline earth oxide, it is essential to remove adsorbed molecules such as carbon dioxide, adsorbed organic matter and water. The catalyst activities of metals depend mainly on the pretreatment temperature and time. When pretreatment temperature was low (below 600 ^{o}C), the catalyst showed as low as 11% yield. The activity increased with increase in calcination temperature, optimizing at 800 ^{o}C and declined with higher pretreatment temperatures.

This calcination effect, coupled with the rearrangement of the surface structure of the mixed oxides in anorthite clay at prolonged pretreatment temperatures for 4 h, resulted in the formation of sufficient acid centers needed for the transesterification of high FFA crude karanj oil (CKO) with methanol. From TGA-DTA result (not shown), the depression at 250 ^{o}C indicate the evolving of adsorbed CO$_2$ and H$_2$O molecules, while the prolonged thermal treatment of catalyst to 800 ^{o}C for 4 h was necessary to generate stronger basic and acid sites. As pretreatment temperature increased, desorption of adsorbed molecules such as carbon dioxide occurred and oxygen anions became available for the reactants. Desorption of adsorbed molecules started from weaker basic sites and more severe pretreatment was required to generate stronger basic sites. At the same time, pretreatment at higher temperature caused the rearrangement of the surface structure of catalyst to more active phases. These two factors induced complex dependence of the catalytic activities with pretreatment temperature.

Tests of activities of catalysts using CKO

The catalytic activities of both the raw and calcined calcium feldspar-derived catalysts, (CaF-Raw and CaF-800), were tested in the transesterification of high FFA crude karanj oil (CKO) for the production of fatty acid methyl ester (FAME). Since the main objective of this work was the production of fatty acid methyl ester at reduced cost, the reaction temperature was kept constant at methanol reflux temperature of 65 ^{o}C while no chemical modification of the catalyst was considered. Varying the reaction time from 0.5 -7 h; but under similar reaction conditions of 6 % (w/w) catalyst loading and methanol/ oil mole ratio of 9:1, it was generally observed that the FAME yield using the raw catalyst was far below 10 % while those of thermally pretreated catalysts improved with increase in calcination temperatures from 500 - 800 ^{o}C (Fig. 3). The catalyst calcined at 900 ^{o}C gave a lower FAME yield than that at 800 ^{o}C. This trend agreed with the work by Boro and co-workers [20] . The poor catalyst performance below 700 ^{o}C was attributed to the inhibition of the catalyst active centers by adsorbed molecules like CO$_2$, H$_2$O, SO$_2$, PO$_4$ and other volatile matter present in the raw catalyst (CaF-Raw). The improved activity observed with increasing calcination temperatures was attributed to the gradual but steady evolving of the adsorbed molecules with steady increase of the active centers.

Effect of methanol/oil mole ratio

Investigating the effect of methanol to oil mole ratio on FAME yield, 6 wt% of catalyst loading was used at 4 h reaction time and at a stirring rate of 700 rpm while methanol /oil mole ratio was varied from 6:1, 9:1, 12:1, 15:1 and 18:1. Although stoichiometrically, transesterification of 1M of oil required 3M of alcohol, excess of alcohol improved conversion.

From the result of transesterification in Fig.4, it could be observed that FAME yield increased initially with increasing methanol to oil ratio to a maximum at 9:1 which gave a FAME yield of 98.97% after 4 h. Further increase from 12:1 - 15:1 gave no significant increase in FAME yield. Hence, for a 6 wt% CaF-800 catalyst loading, 9:1 oil to methanol mole ratio was sufficient for good yield. A higher ratio would therefore be wasteful. Also, poor phase separation between the fatty acid methyl ester and glycerol by-product was observed when higher methanol to oil mole ratio was used.

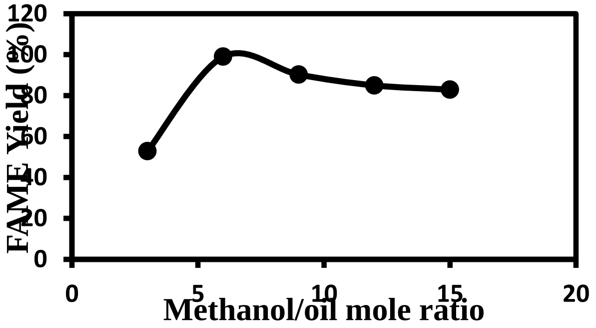

Fig. 4: Effect of methanol/oil mole ratio on catalyst activity (catalyst loading/oil weight ratio – 6 wt%; reaction temperature 65 ºC; reaction time 4 h and stirring speed 700 rpm).

Effect of catalyst loading

The effect of catalyst loading was tested for the transesterification of CKO using 9:1 methanol/oil mole ratio and 4 h reaction time at 700 rpm stirring rate while catalyst loading was varied from 3- 9 % by wt. kg^{-1} oil.

A close observation of Fig.5 revealed an increase in FAME yield to a maximum of 98.97% obtained for 6 wt% after 4 h reaction time. Further increase in catalyst loading beyond 6 % by wt. showed no appreciable increase in FAME yield.

The observed low FAME yield below 6 % by wt. catalyst loading could be attributed to insufficient availability of catalyst active surface needed to drive the reaction for efficient conversion. Above 6 % by wt., the reactants formed a viscous emulsion which limited the mass transfer of components to the catalyst active surface causing saturation and diffusion effects which hindered interaction. This effect caused the observed decline in FAME yield beyond 6 % by wt.. Therefore, further increase of catalyst beyond 6 % by wt. would amount to waste of valuable resource.

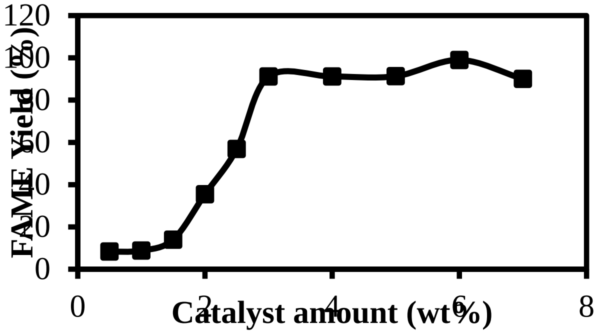

Fig. 5: Effect of catalyst loading on FAME yield of crude karanj oil (methanol/oil mole ratio 9:1; reaction time 4 h; reaction temperature 65 ºC and stirring speed 700 rpm).

Effect of reaction time

To evaluate the effect of reaction time on FAME yield, other operational parameters such as catalyst loading (6 % by wt.), methanol to oil mole ratio (9:1), methanol reflux temperature were kept constant while duration of reactions were varied from 0.5 - 7 h.

It could be observed from the graph that the highest FAME yield was recorded after 4 h reaction time for CaF-800 with a yield of 98.97%. The FAME yield could scarcely hit 50 % after 2 h reaction time. However, a steady increase in conversion of triglycerides was observed until an optimum of 98.97% after 4 h duration. No further significant increase in FAME yield was observed with prolonged reaction time. Hence, under the present reaction conditions, prolonged reaction beyond 4 h reaction time would mean a waste of energy.

Conclusion

Non-edible, crude karanj (Pongamia pinnata) oil (CKO) with high FFA has been identified as potential renewable, low cost feedstock for the production of FAME. Whereas many currently known base heterogeneous catalysts were destroyed by high free fatty acids content in feedstock, the calcium feldspar catalyst system has been shown here to excellently convert high FFA CKO directly to fatty acid methyl ester (FAME). This was attributed to the conversion of some metal oxide content of the clay catalyst to acidic mesoporous aluminium silicate mixed oxide centers by prolonged calcination. The clay material also functions as mesoporous sieve to help facilitate conversion. The best FAME yield (> 98.97 %) was obtained at methanol reflux reaction temperature, 6 % by wt. catalyst loading, methanol to oil mole ratio of 9:1 after 4 h reaction time.

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